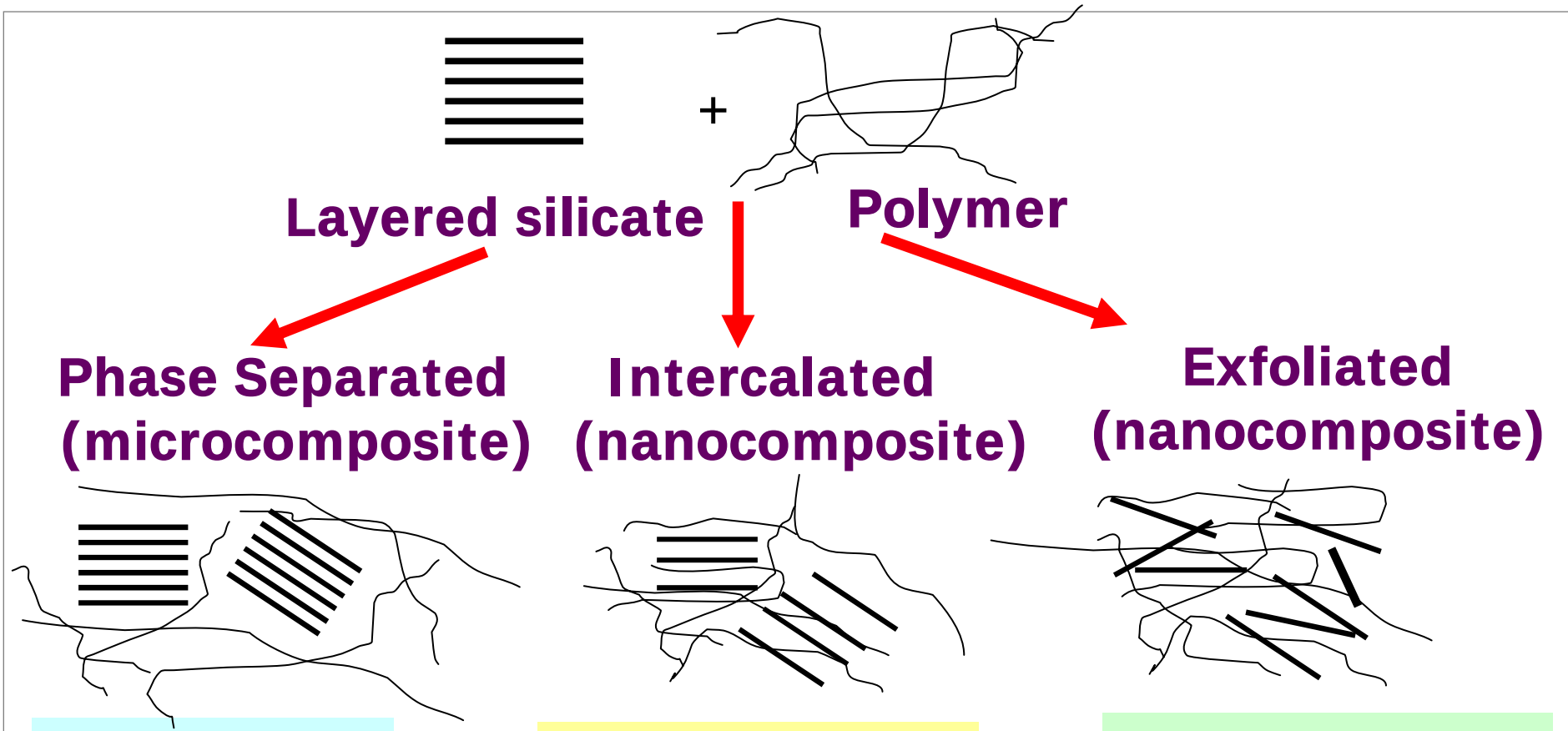
New Fire Retardant Fillers based on Modified Organoclays

Pranav Nawani, Mikhail Y. Gelfer, Priya Desai
And Benjamin S. Hsiao

Departments of Chemistry
Stony Brook University

Annual Fire conference April 3-4 2006, NIST

Polymer-Clay Nanocomposites



Clay and Polymer Structures → Clay Particles in Polymer Matrix → Properties of Composites at Molecular Level

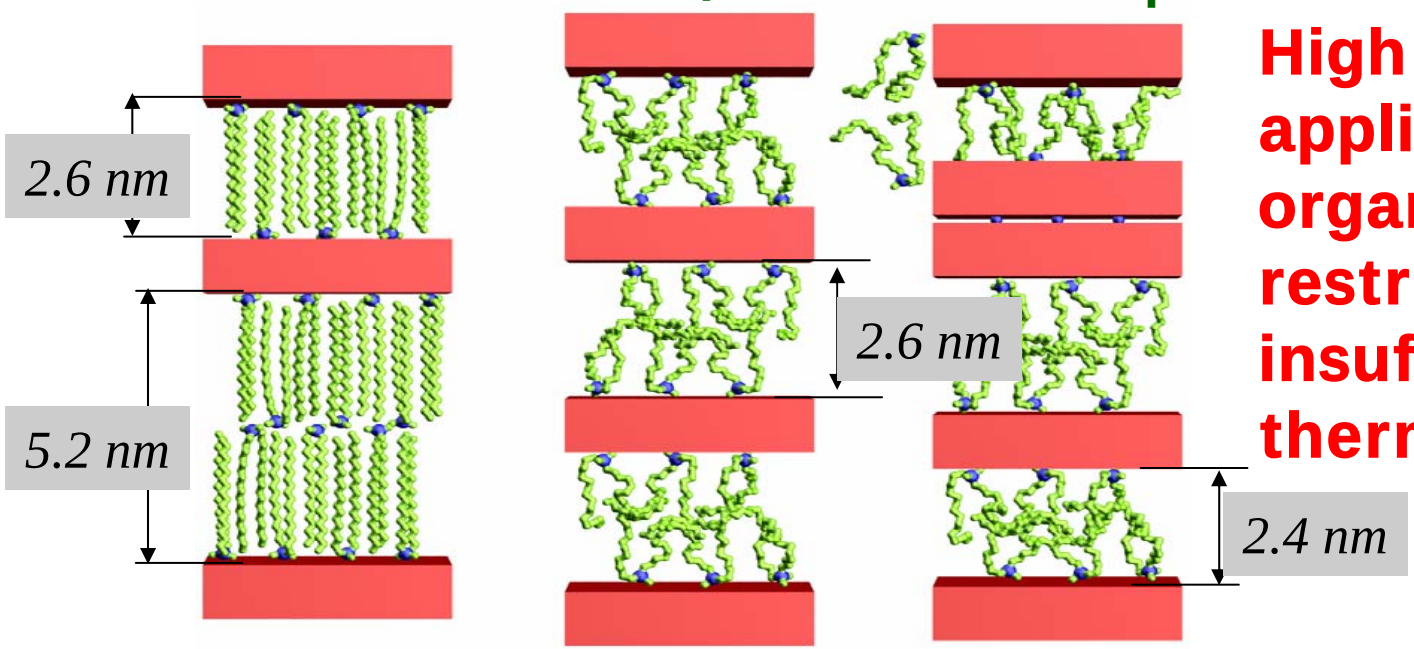
Morphology of Cloisite Organoclay

Organically modified layered silicates (organoclays) are known to improve FR activity of polymers

30°C
Bimodal thickness distribution

100 - 180°C
Unimodal thickness distribution - **double layers collapse**

200 -260 °C
Degradation, surfactant loss - **organic layers collapse**



High temperature applications of organoclays restricted by insufficient thermal stability

***Langmuir 20*, 3746-3758 (2004)**

STONY BROOK UNIVERSITY

Hence a need to develop organoclays with increased thermal stability

We propose transition metal ions (TMI) modification of organoclays

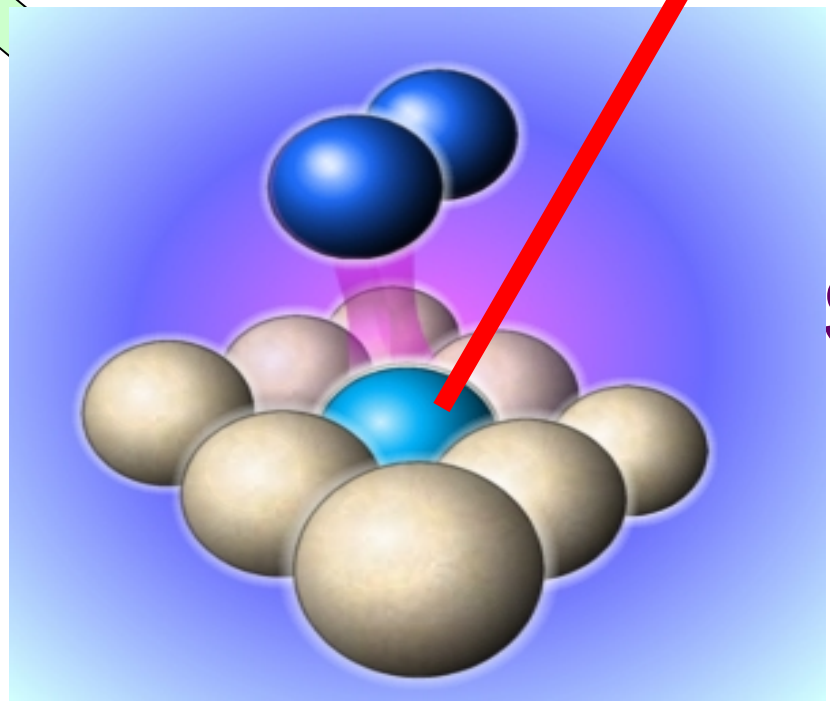
Why TMI (e.g. Fe and Cu)

STONY BROOK UNIVERSITY

- TMI in the organoclay (organic components)
  - May promote chemical cross-linking, oxidative dehydrogenation and charring (chemical action)
- In polymer matrix
  - May promote chemical cross-linking, oxidative dehydrogenation and charring (chemical action)
  - Drastically increased viscosity at high temperatures, reduce gas permeability (physical action).
- Fe and Cu
  - Easy availability; well known solution chemistry

Modification of organoclays

Active catalytic sites



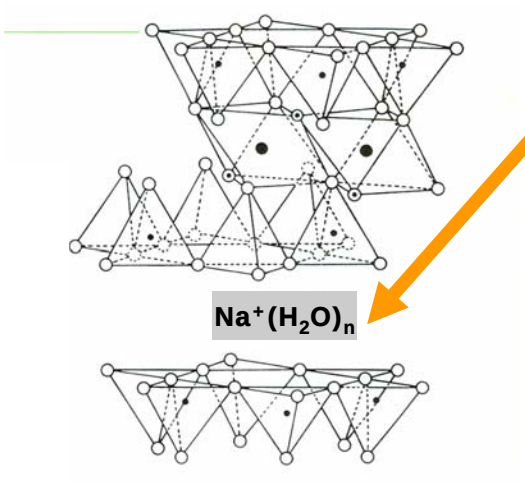
sis

Catalysis is the key

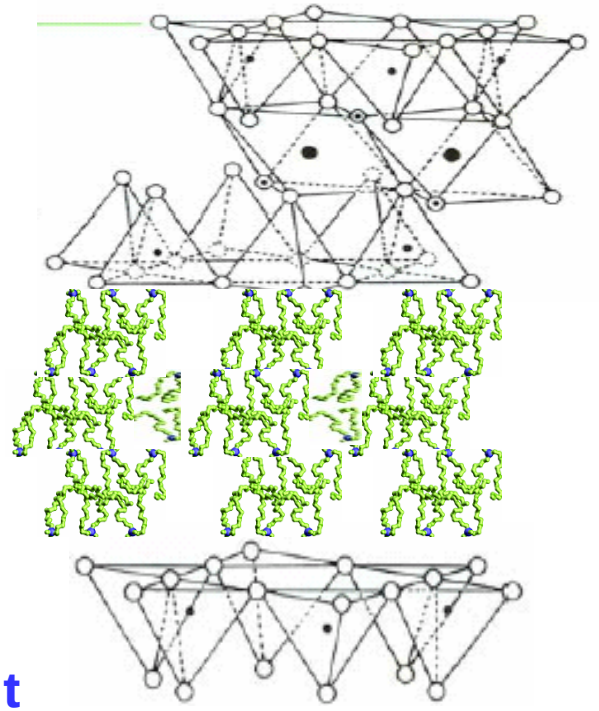
Increase in thermal stability and FR properties of composites

http://edu.chem.tue.nl

Chosen Materials



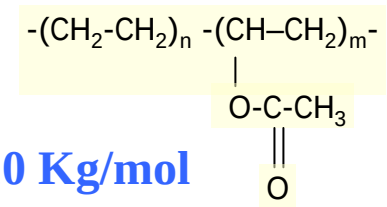
Interlayer ions in typical montmorillonite mineral clays
***d* = 1 to 2 nm**



Surfactants in interlayer region of C20A organoclay
***d* = 1 to 3 nm**

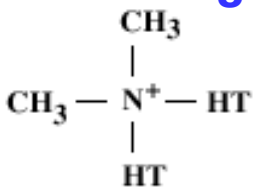
Ethyl vinyl acetate EVA8

contains - 8% mol. vinylacetate;



M_w= 110 Kg/mol

Typical surfactant present in organoclays

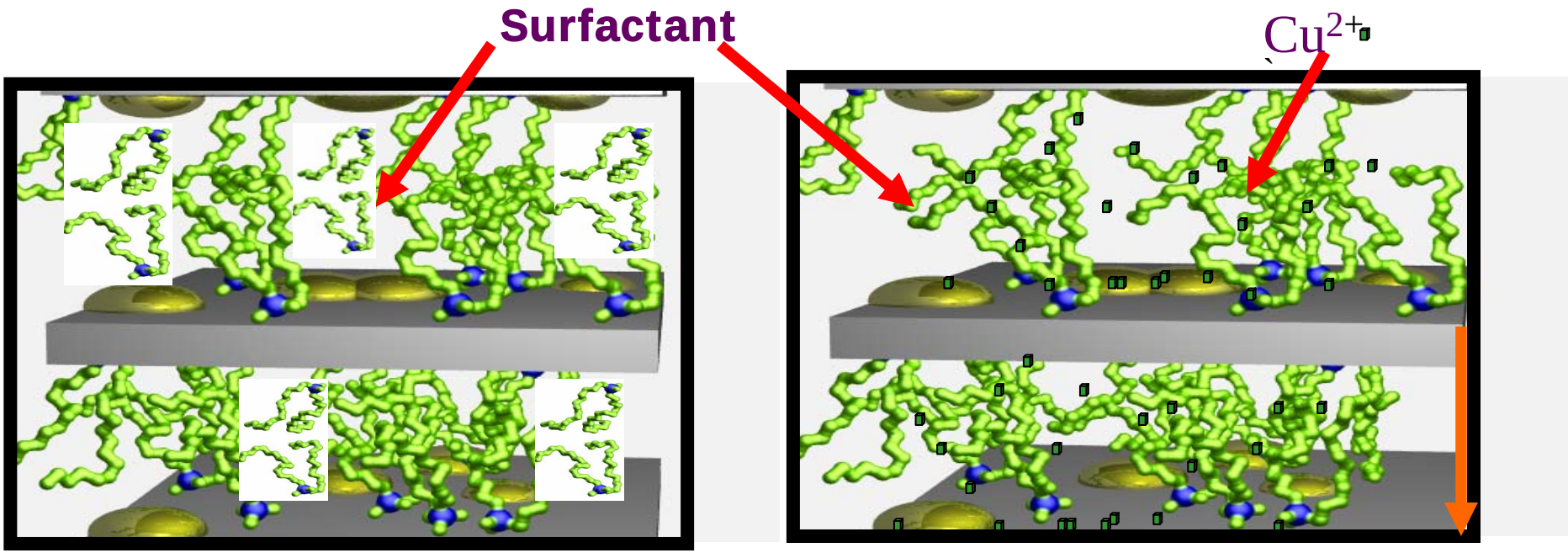


2M2HT: dimethyl, dihydrogenatedtallow quaternary ammonium chloride
wt% ~35% in C20 A

Transition metal ions slats (chlorides) and solvent like methanol etc.

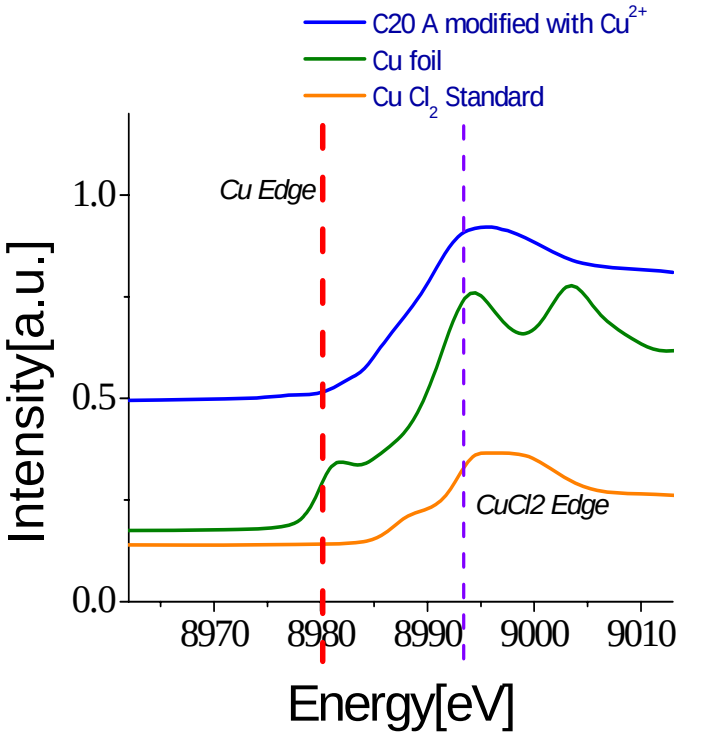
Modification of Organoclays

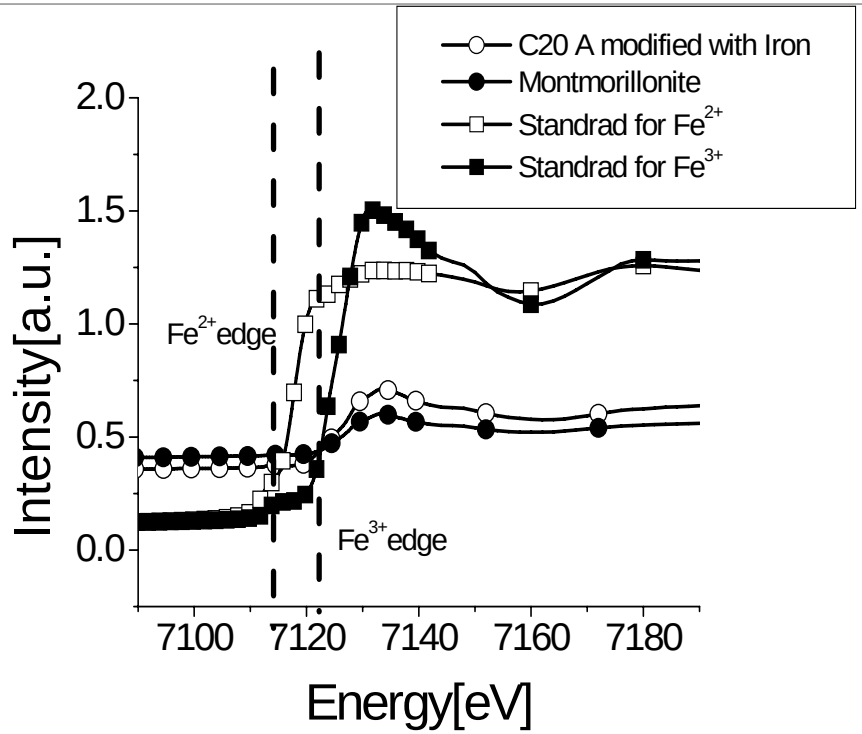
- Pre-washing with desired solvent
- Modification by TMI solution



Surfactants are lost when ion exchanged with TMI

Oxidation state of TMI in Clay



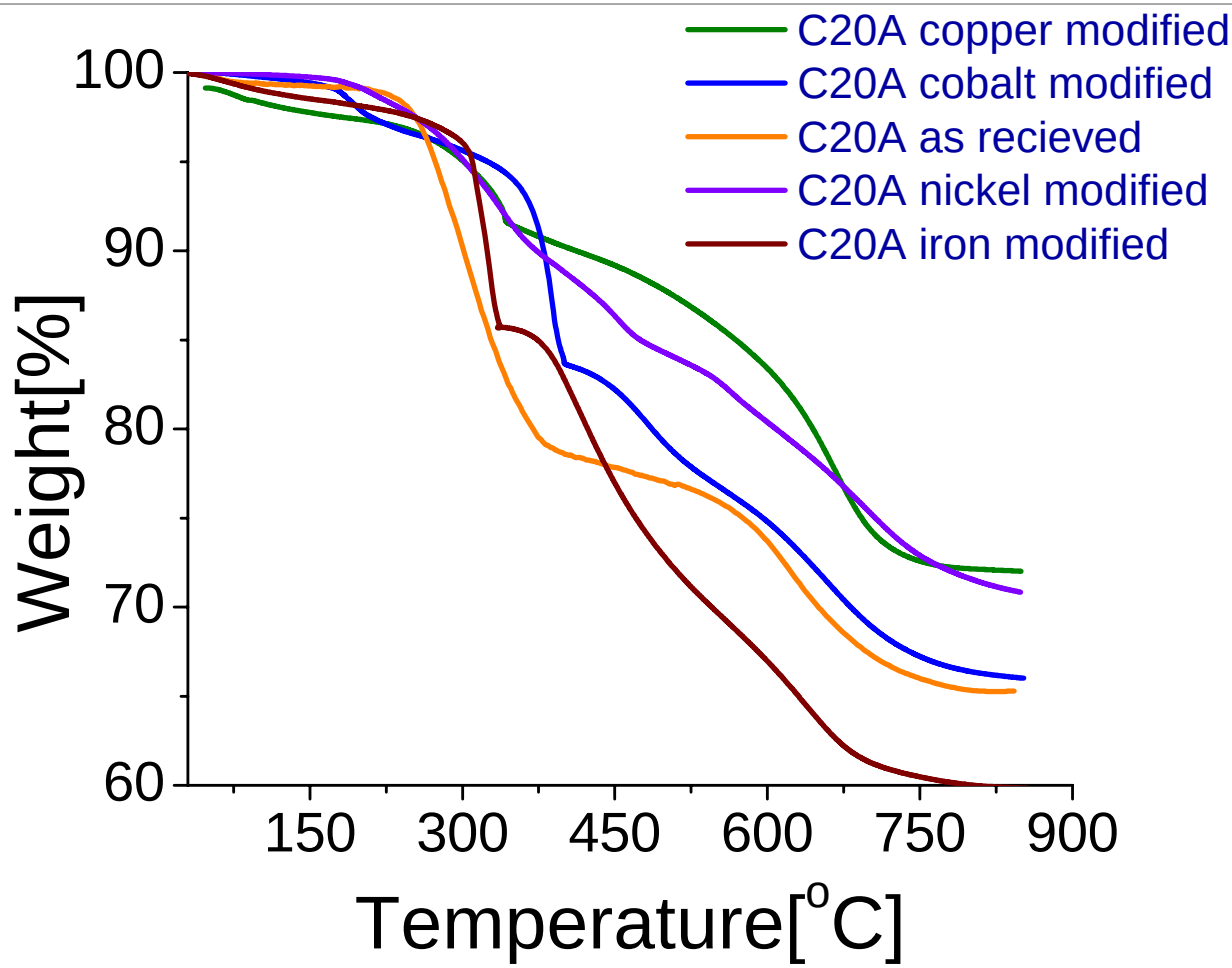


Cu^{2+}& Fe^{3+}edge shifted to lower E in copper modified clays

Cu^{2+}& Fe^{3+} is partially reduced => mixture of different oxidation state

TMI exist in more than one oxidation state in organoclays they might form complex with surfactants

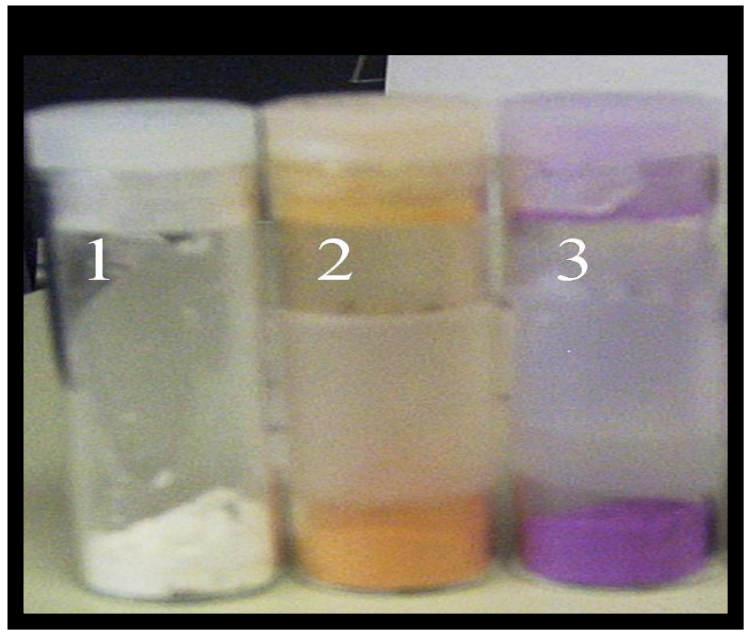
TMI and thermal stability



In presence of TMI thermal stability of organoclays increases and onset in presence of Cu is highest

Reduction of Organoclays

- Reduction of TMI in gallery of silicates using sodium borohydrate.
  1) C20A, 2) C20A-Fe and 3) C20A-Cu



Change of color with addition of sodium borohydrate is indicative of reaction

Characterization Techniques

STONY BROOK UNIVERSITY

- Elemental Analysis (EA)
- Scanning and Transmission electron microscopy (SEM & TEM)
- Thermo gravimetric analysis (TGA)
- X-ray scattering
  - SAXS / WAXD
- Extended X-ray Absorption Fine Structure (EXAFS)
- Flammability tests
  - LOI and UL-94

Results

Elemental Analysis (wt%)

Material Analyzed	Montmorillonite	Montmorillonite - Cu	C20 A	C20 A washed	C20A Cu	C20A Fe
C						.11
Hy						.20
Ni						.84
C						.00
Chlorine	0.00	<0.1	0.00	0.00	3.50	<0.1
Iron	0.90	0.93	1.74	1.56	0.94	4.13
Sodium	4.17	0.19	<0.5	<0.5	0.00	0.00

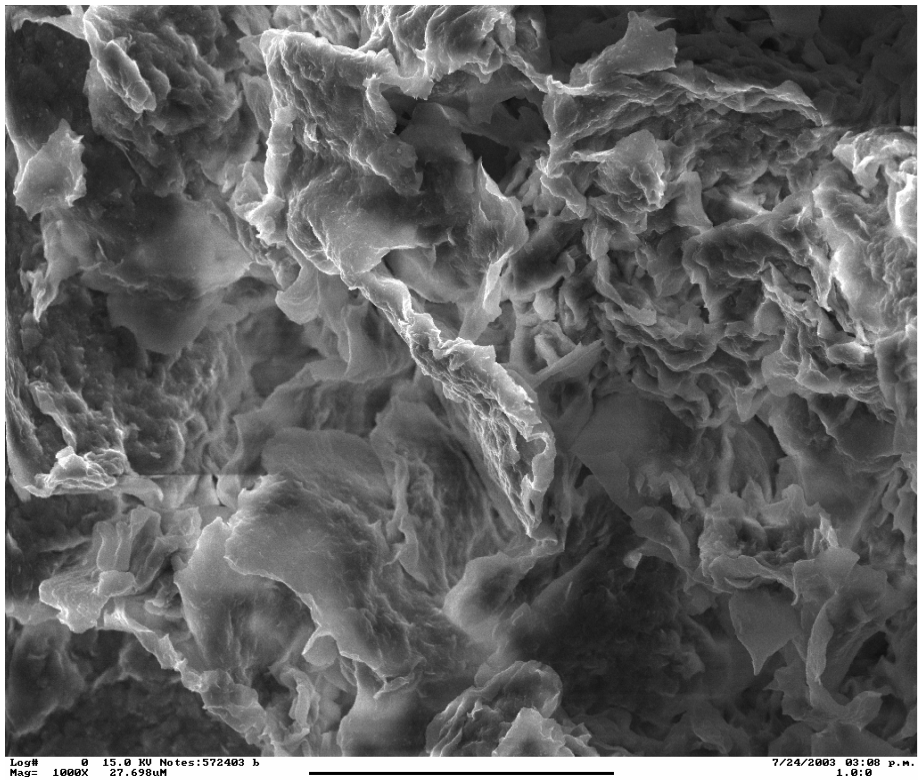
Solvent may be trapped in montmorillonite

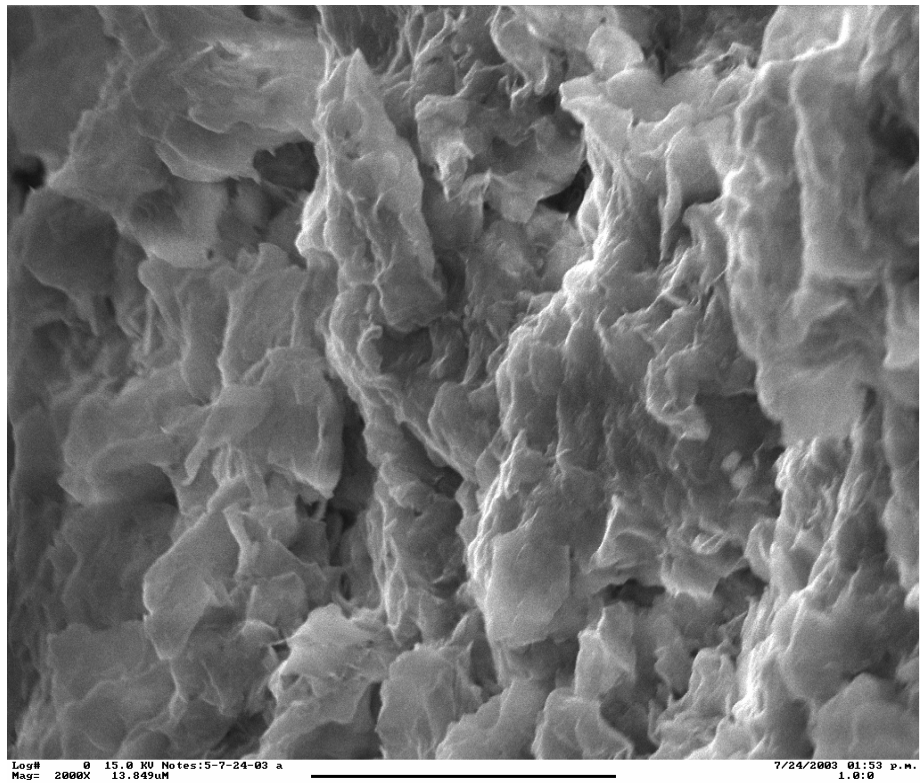
Structural iron in montmorillonite and non structural iron in C20A

Cu may be reduced and CuCl may be trapped

Schwarzkopf Microanalytical Lab, Inc., (Queens, NY).

SEM





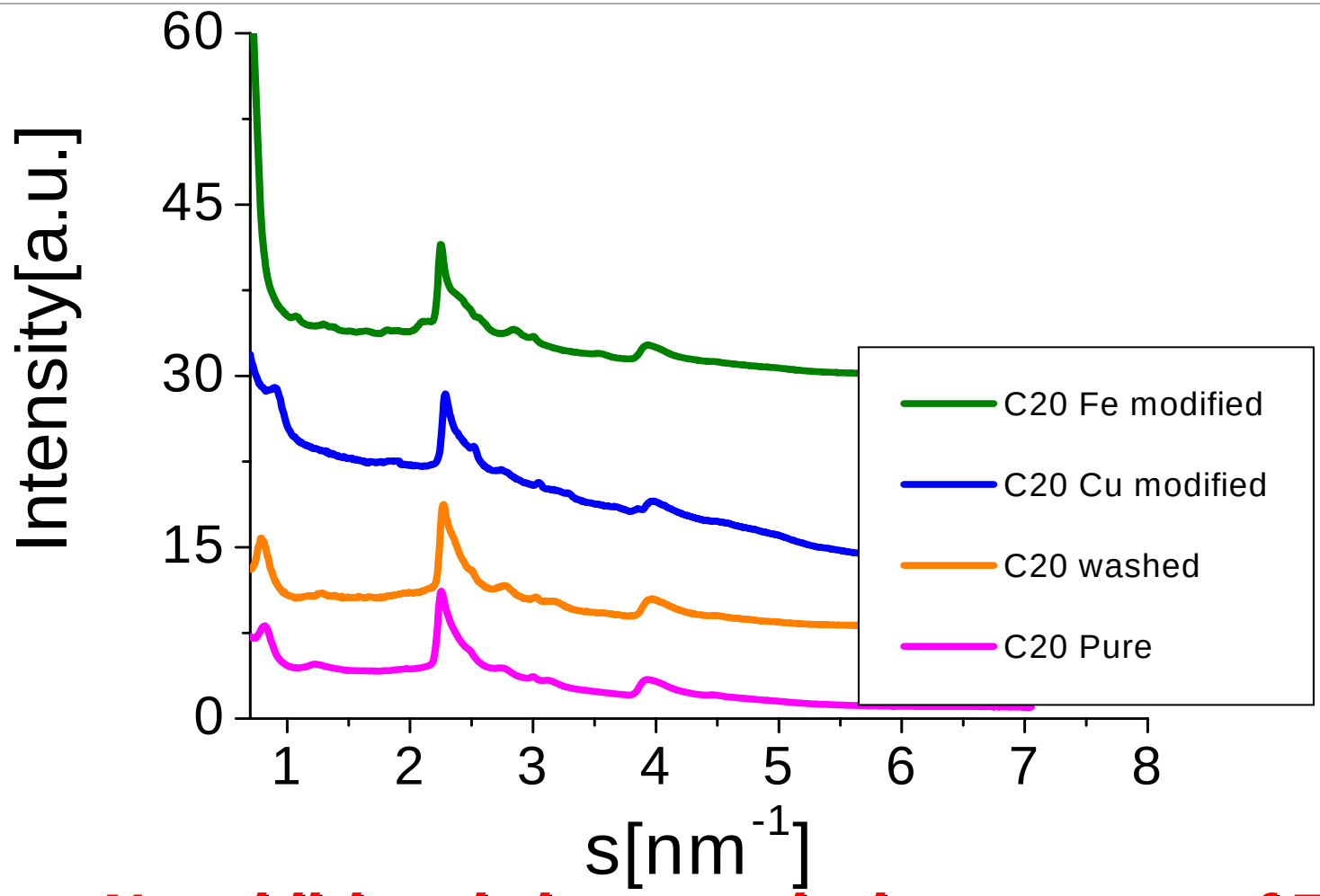
Organoclay C20A as received

~15 μm

Organoclay C20A modified with copper

No deposits of TMI on the surface of closite
Similar results were obtained for other TMI

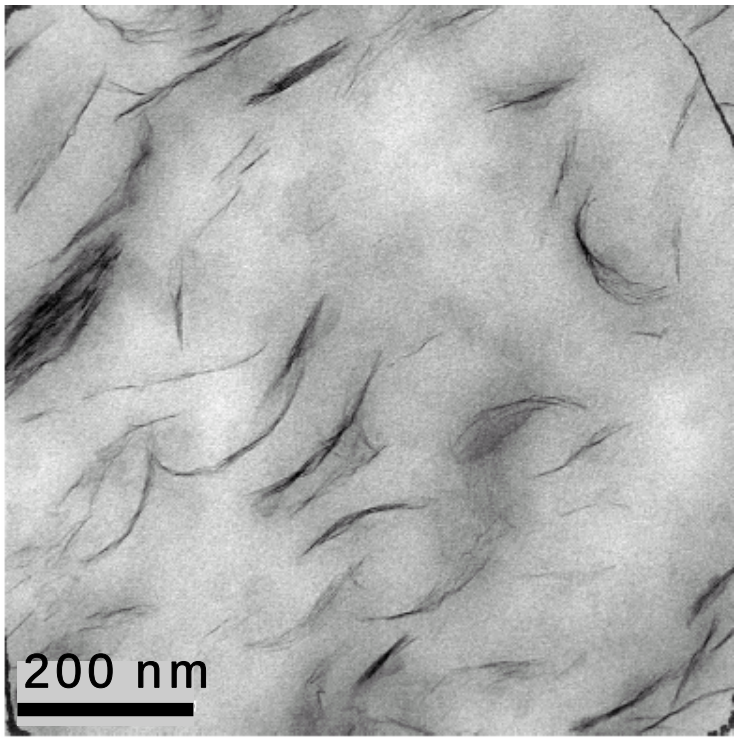
WAXD of C20A Organoclay



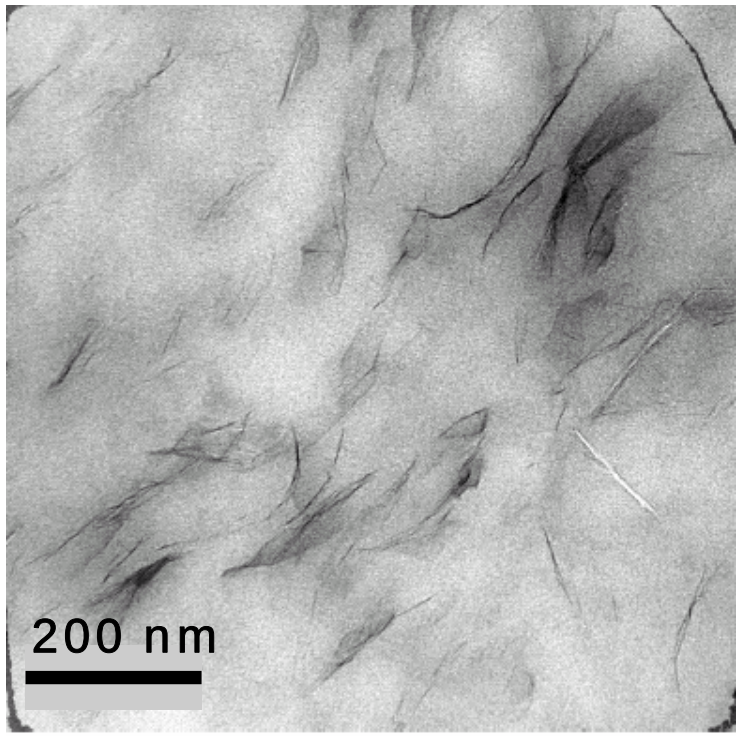
No additional sharp peaks in presence of TMI

TMI is not deposited on surface of clay stacks

TEM



EVA 350 C20A 10wt%



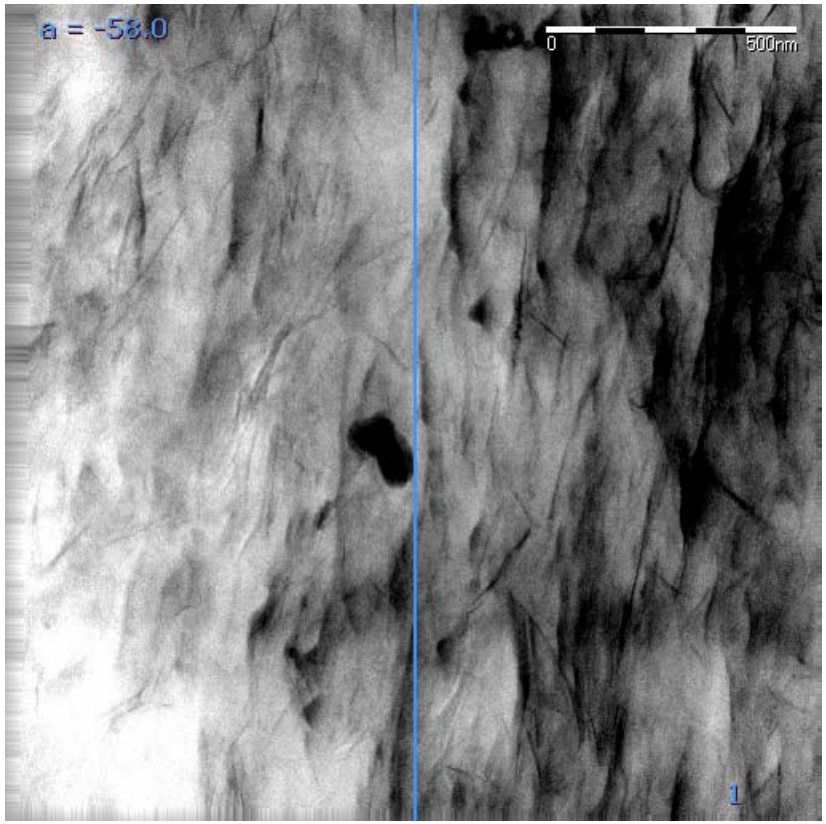
EVA 350 C20A Cu 10 wt%

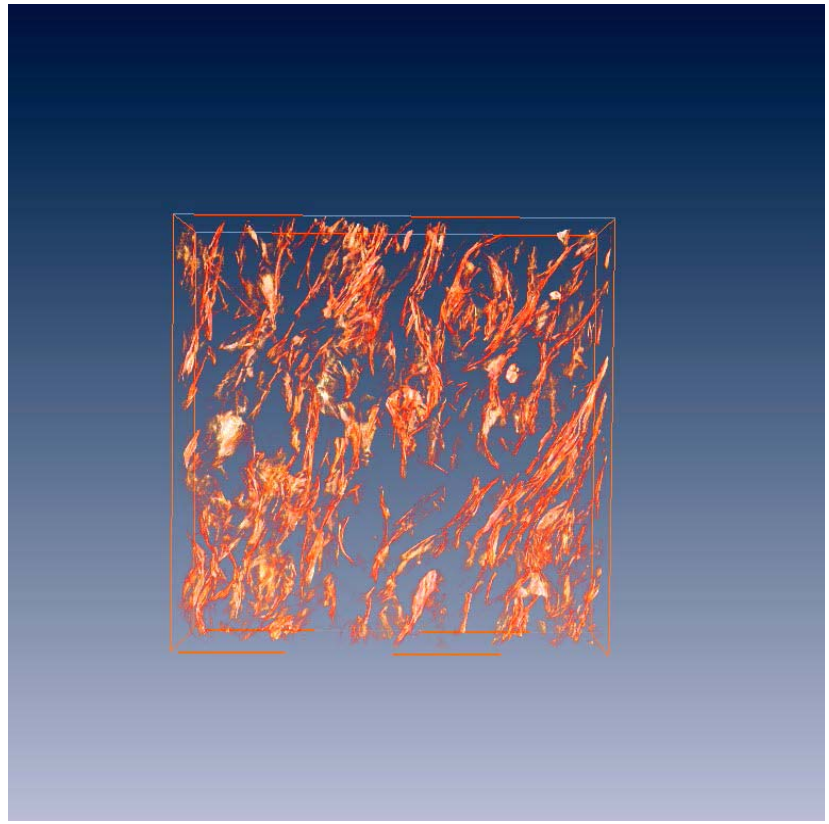
No aggregation is observed indicating dispersion remains homogeneous even for TMI modified clays

Clay tactoids break suggesting intercalated-exfoliated mix

3D - TEM

EVA 350 C20A Cu10wt%



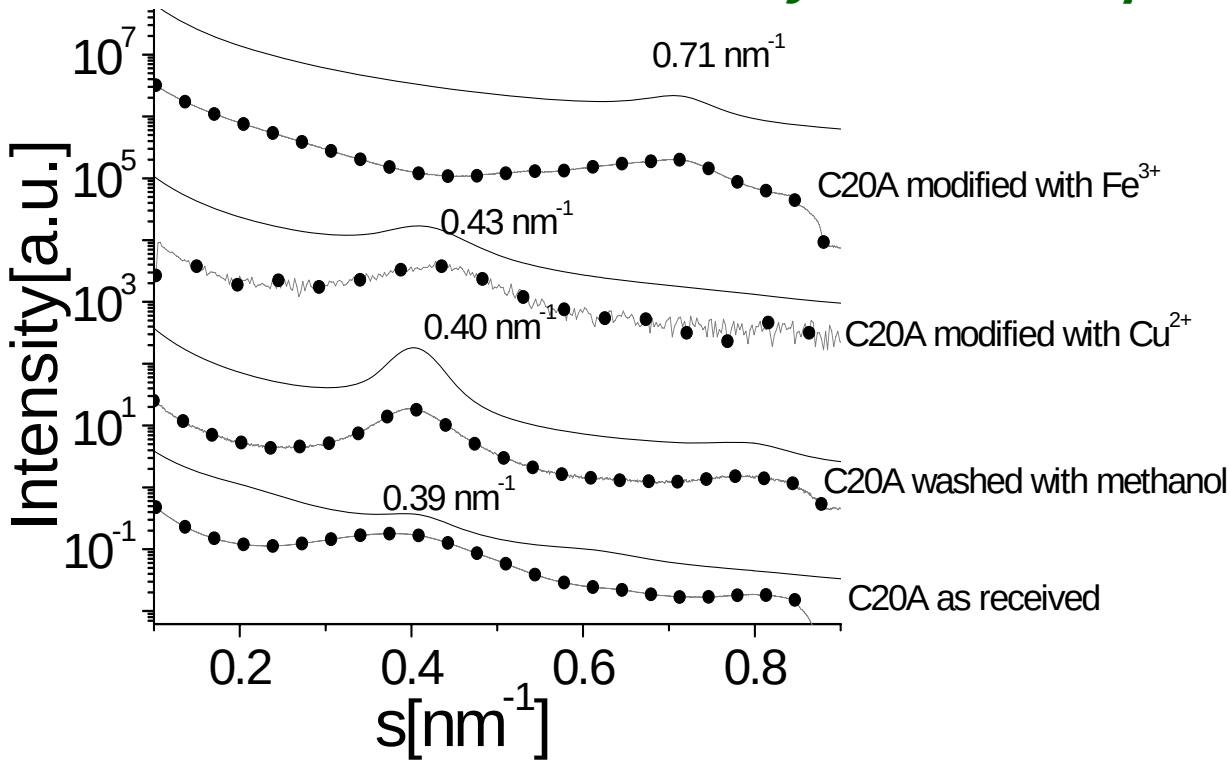


No deposits of TMI on the surface of closite
Similar results were obtained for other TMI

Structure Analysis by SAXS

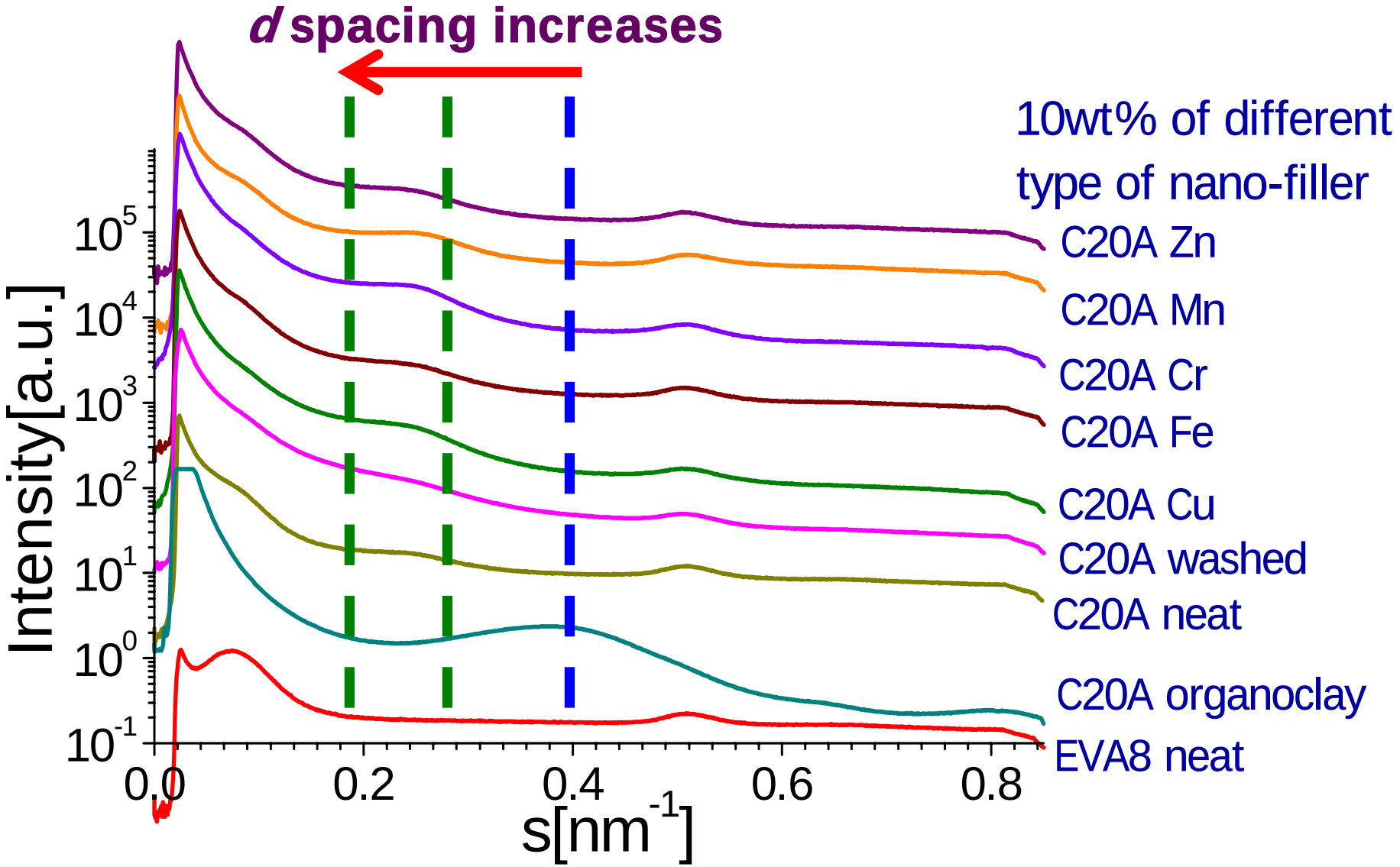
C20A organoclay modified with various TMI (Cu^{2+} and Fe^{3+}) compared with that of C20A as received and washed with methanol.

Solid line is for calculated and lines with symbols are experimental data.



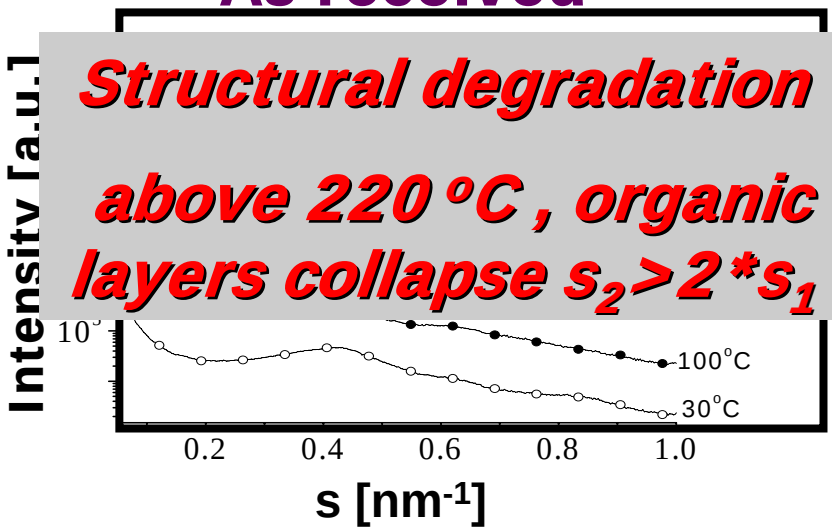
Shift in d- spacing indicates intercalation of TMI takes place within the layers of clays

SAXS trace for composites



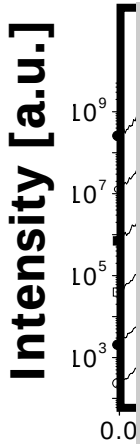
SAXS trace for clay

As received



Structural degradation above 220 °C , organic layers collapse $s_2 > 2*s_1$

Methanol Washed

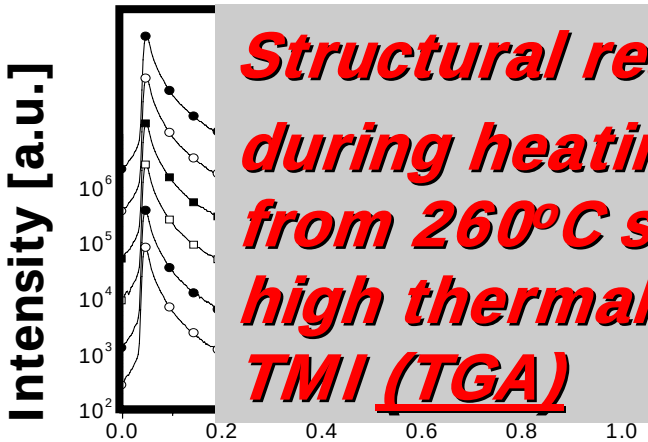


Structure remains stable to 260°C

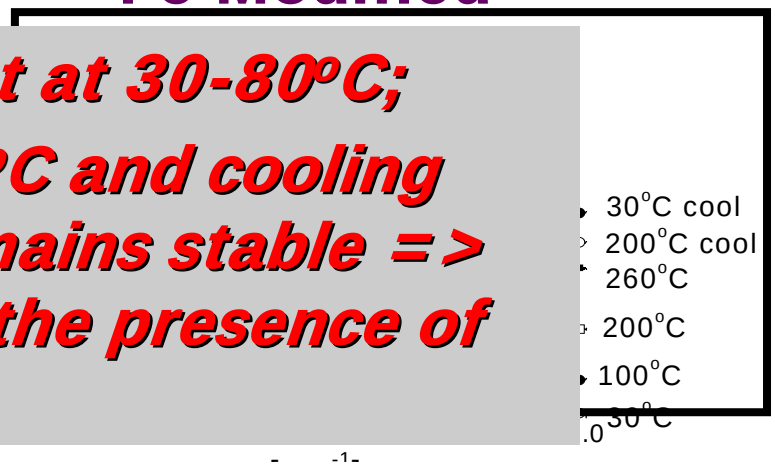
$s_2 = 2 * s_1$

Reversible upon cooling

Cu modified



Fe Modified



Structural rearrangement at 30-80°C; during heating above 80°C and cooling from 260°C structure remains stable => high thermal stability in the presence of TMI (TGA)

X-Ray Results

STONY BROOK UNIVERSITY

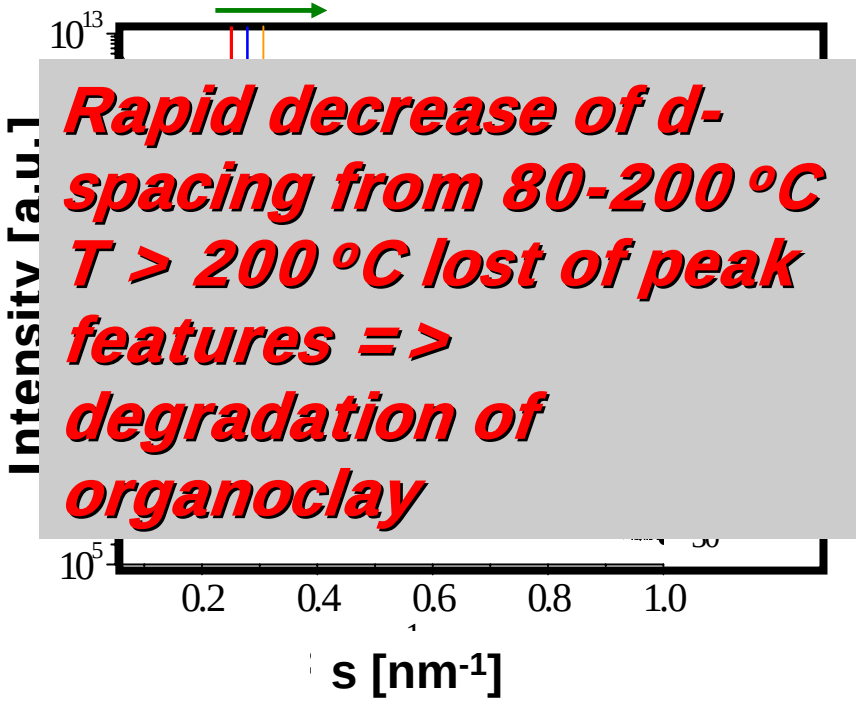
- *d*-spacings change
  - TMI ions penetrate into the interlayer region
  - *d-value* may be affected by status of TMI (ions, aggregates, reduction, colloid particles or complexation of TMI)
- Improved thermal behavior in TMI modified Cloisite, hence we can say TMI helps in improving thermal stability.
  - Similar results obtained from TGA thermograms.

SAXS trace for composites

STONY BROOK UNIVERSITY

As received

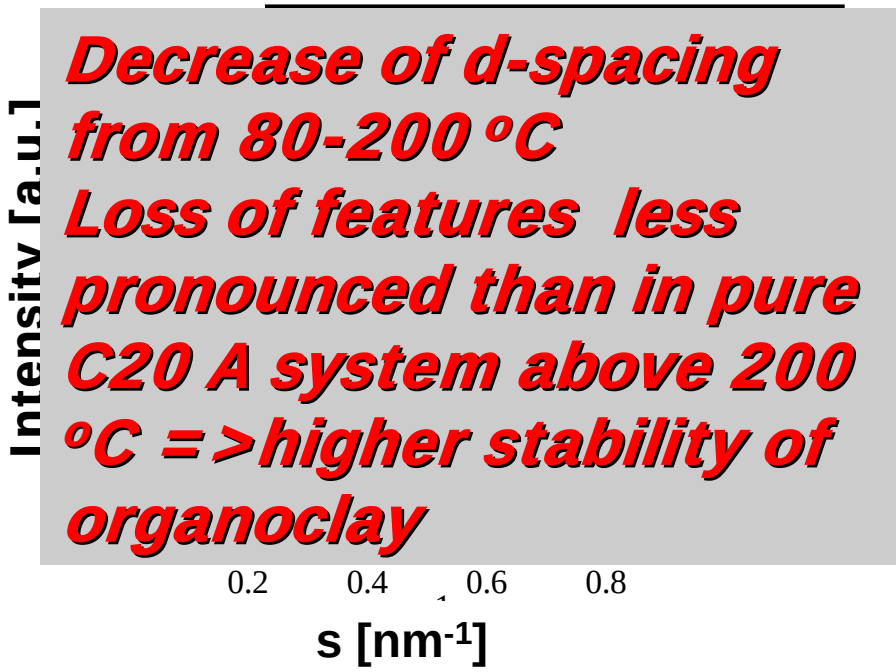
d-decreases



Rapid decrease of d-spacing from 80-200 °C T > 200 °C lost of peak features => degradation of organoclay

Cu modified

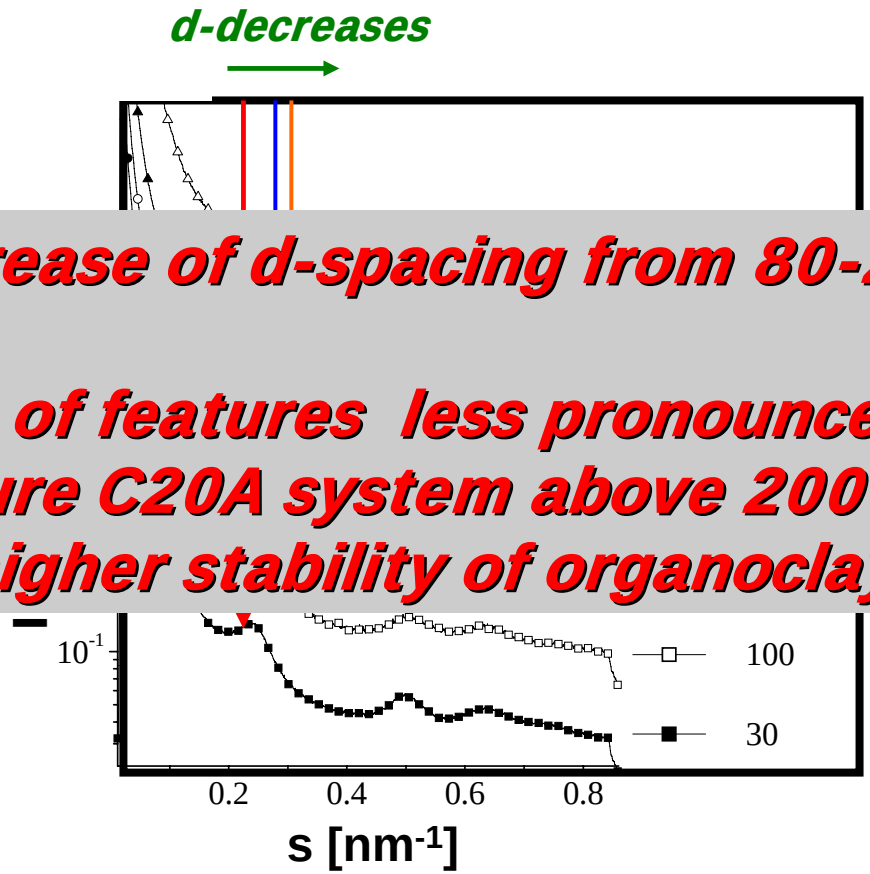
d-decreases



Decrease of d-spacing from 80-200 °C Loss of features less pronounced than in pure C20 A system above 200 °C =>higher stability of organoclay

SAXS trace for composites

Fe Modified



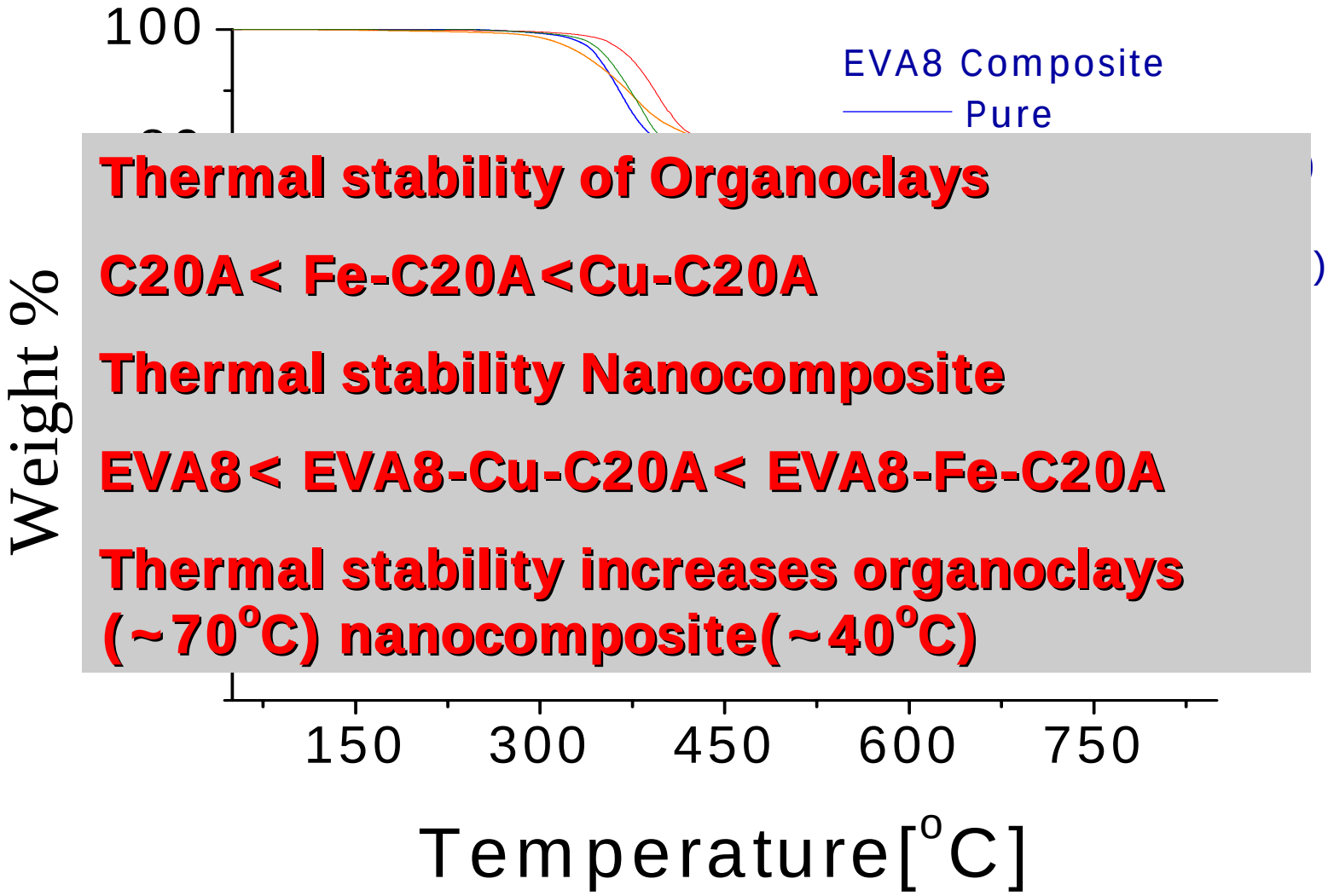
Decrease of d-spacing from 80-200 °C;

Loss of features less pronounced than in pure C20A system above 200 °C
=>higher stability of organoclay

X-Ray Results

- *d*-spacings changes and peak broadens
  - Intercalation takes place
  - Partial exfoliation possible
- Improved thermal behavior in TMI modified Cloisite EVA composites,
  - Hence we can say TMI helps in improving thermal stability.
- Similar results obtained from TGA thermograms.

TGA data for nanocomposite



Thermal stability of Organoclays

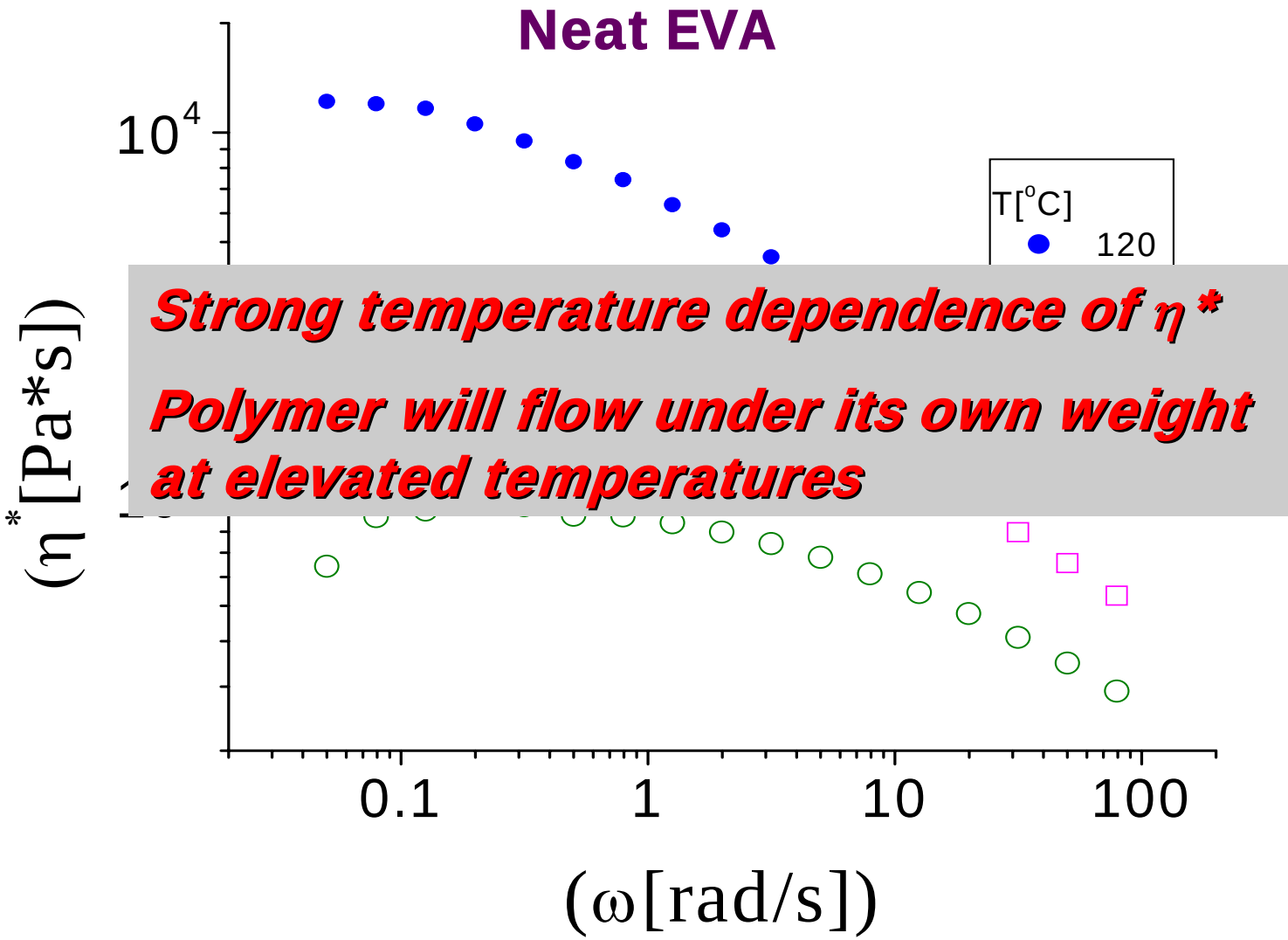
C20A< Fe-C20A<Cu-C20A

Thermal stability Nanocomposite

EVA8< EVA8-Cu-C20A< EVA8-Fe-C20A

Thermal stability increases organoclays (~70°C) nanocomposite(~40°C)

Rheological Measurements



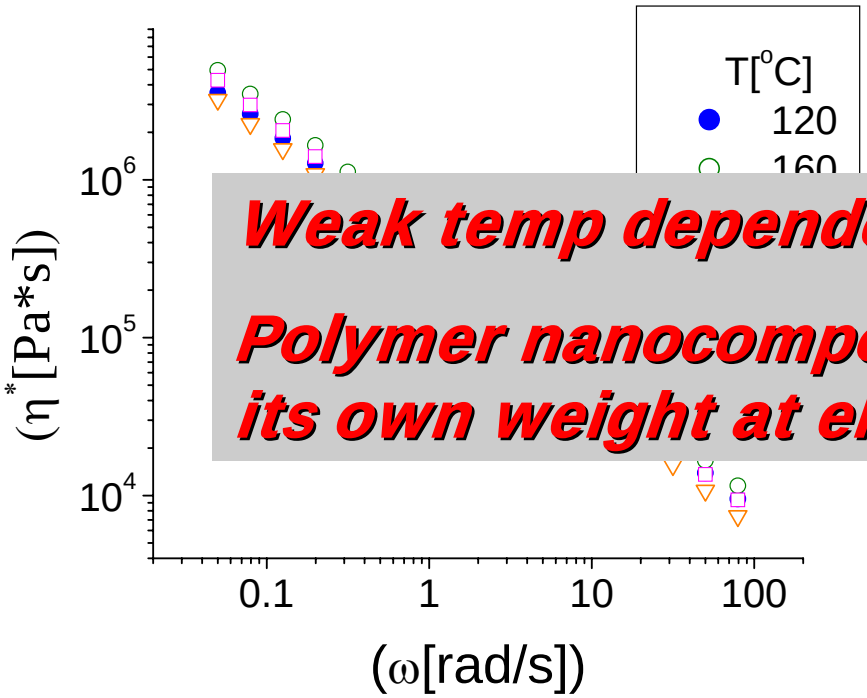
Strong temperature dependence of η*

Polymer will flow under its own weight at elevated temperatures

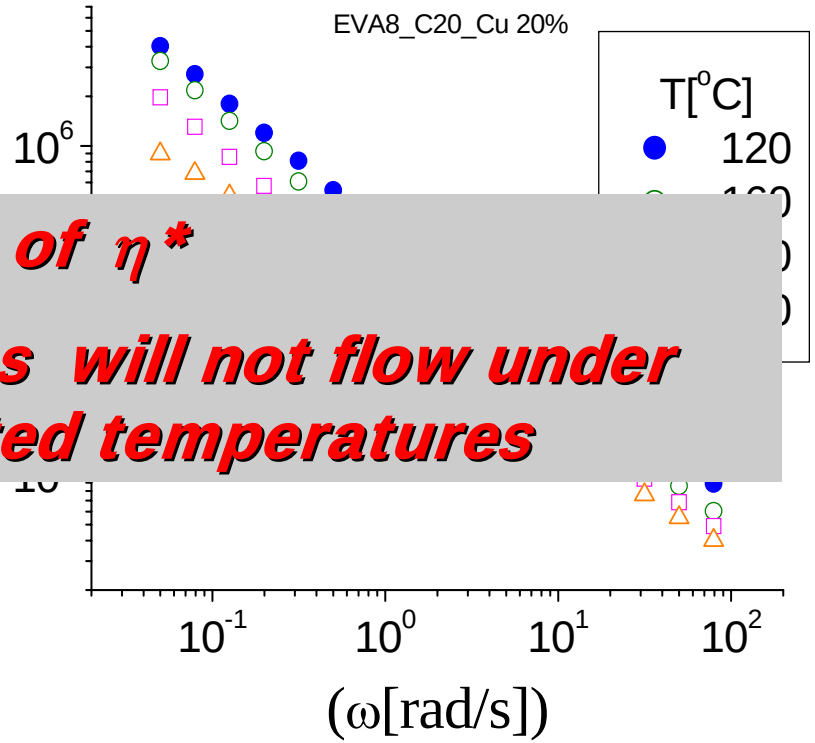
Rheological Measurements

STONY BROOK UNIVERSITY

EVA Pure C20A 10 %



EVA Cu modified C20A 10 %



Weak temp dependence of η*

Polymer nanocomposites will not flow under its own weight at elevated temperatures

Test of Flammability: LOI

	Oxygen Index values	
Sample	0 wt% MgOH	5 wt% MgOH
Eva NEAT	19.19	-
Eva C20A	19.35	20.94
Eva C20A Cu	19.25	19.55
Eva C20A Cu (reduced)	19.25	19.45
Eva C20A Fe	19.72	21.52
Eva C20A Fe (reduced)	19.78	21.63

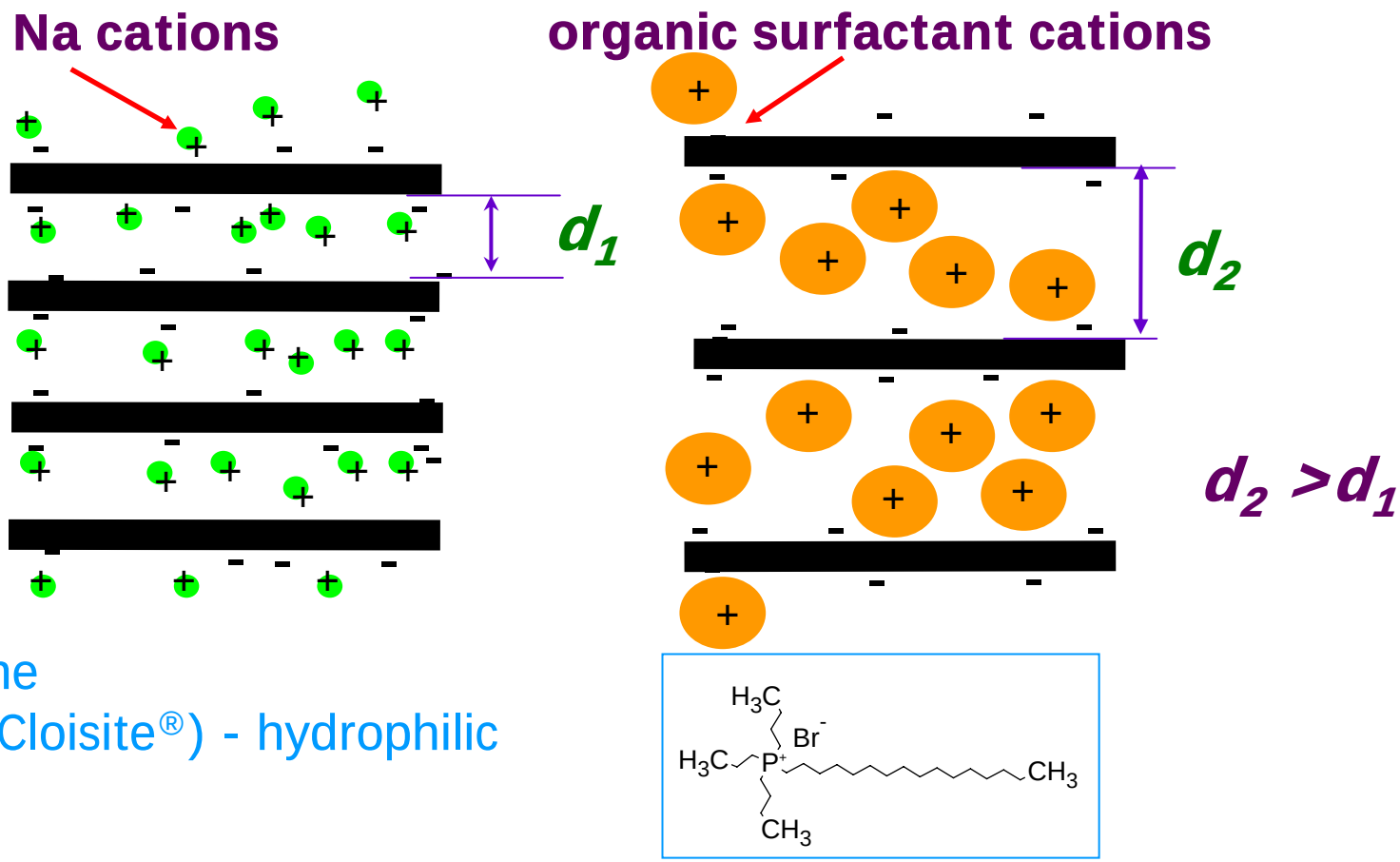
In accordance to our data of SAXS and TGA where Fe modified clay composite showed higher thermal stability

Test of Flammability: UL-94

STONY BROOK UNIVERSITY

Sample (10wt% of filler)	0% MgOH	50% MgOH
Eva NEAT	V2	-
Eva C20A	V1	V0
Eva C20A Cu	V1	V0
Eva C20A Cu (reduced	V1	V0
Eva C20A Fe	V1	V0
Eva C20A Fe (reduced)	V1	V0
Eva Phosphonium	V1	V0
Eva Phosphonium Cu	V0	V0

Preparation of Organoclays by Exchanging Sodium Cations with Surfactant



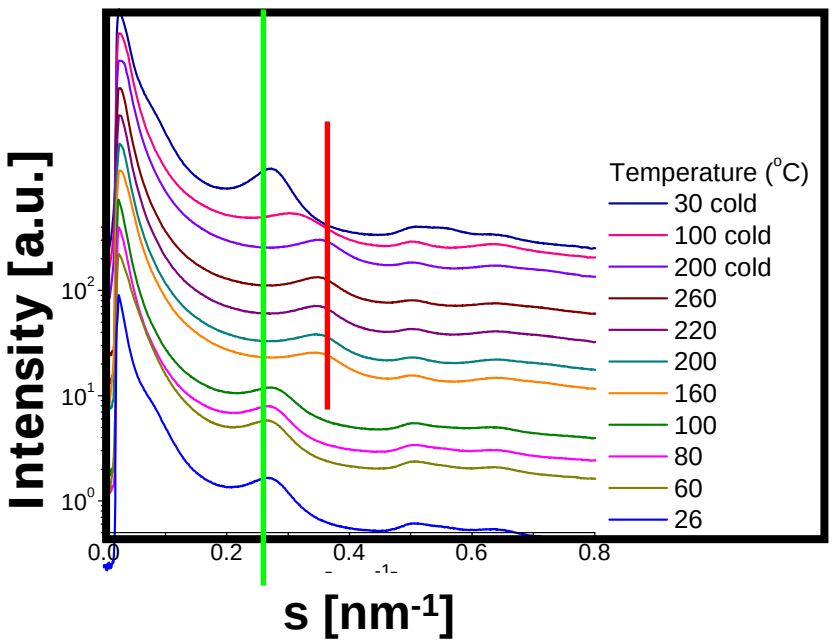
Surfactants: *N, N, N,*-tributyl-*N*-hexadecyl phosphonium bromide3

Phosphonium montmorillonite

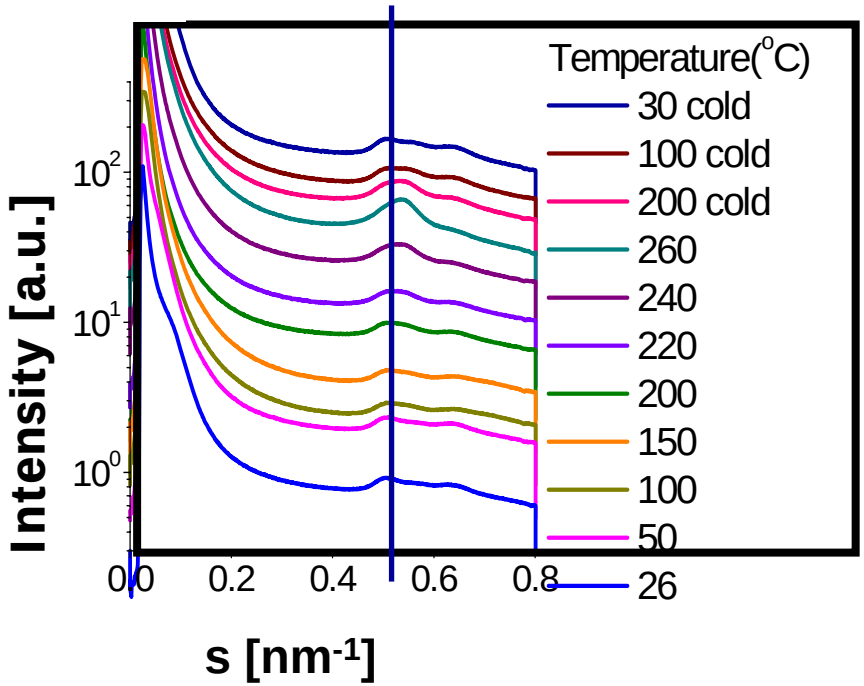
STONY BROOK UNIVERSITY

Clay as made

d-decreases



Cu modified



With TMI (Cu^{2+}) modification , structure is more stable at higher temperatures hence thermally stable filler

Summary

- Efficient modification of organoclays can be achieved by treating them with TMI salt solution
  - SEM, WAXD and SAXS results prove that TMI can be intercalated in organoclays.
- TMI modification result in the shifting of the onset of degradation of organoclays towards higher temperatures, hence thermally stable.
- TMI modified organoclays in EVA matrix may promote cross-linking, high viscosity and charring thus may increase their FR properties.
  - Effect of Fe was more prominent than Cu
- With Phosphonium surfactant montmorillonite was thermally more stable

Future work

- Elucidating the role of structural and non-structural iron.
- Testing synergic blends of TMI-modified organoclays with other additives and conventional FR agents
- Using thermally stable surfactants
- Testing different polymer matrices
- Using the polymer blends for nanocomposite
- Detailed study of SAXS for understanding dispersion of organoclays and polymer nanocomposites

Acknowledgements

- *Lixia and Igors at BNL*
- *Gregory Rudomen, University Microscopy Imaging Center S.U.N.Y Stony Brook*
- *Andy Tsou at Exxon Mobil*

- *Final Support Provided by The Fire Division, National Institute of Standards and Technology*